A Coarse - Grained Rigid Blob Model:
Toward Mesoscopic Nanostructure Simulations

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Objectives and Approach

Our goal: Large - Scale Nanostructure Simulations
Develop a systematic methodology to perform accurate and efficient molecular dynamics simulations for large- and multi-scale materials systems with a number of atoms greater than 10^9 and a time scale longer than 100 *nanoseconds; i.e.,* beyond the present state-of-the-art.

Our approach: Coarse - Grained Rigid Blob Model
(1) Rigid Blob : Average out fast intra-molecular degrees of freedom.
(2) Coarse-Grained Interactions : Represent the inter-blob potential by a multipolar expansion with molecular characteristics.
(3) Molecular Shapes : Preserve molecular symmetries and nonspherical (anisotropic) shapes.
(4) Separated Dynamics : Reduce the full atomistic dynamics to a formally separated translational and rotational dynamics.

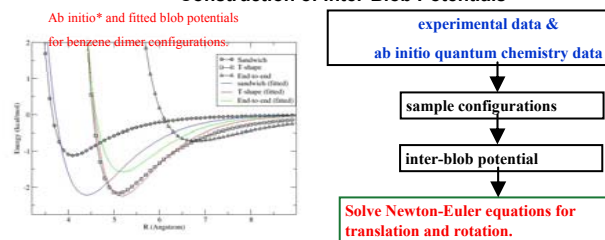## Taylor expansion of inter-blob potential

$$U(r)$$
$$= U(R)$$
$$+ (\vec{\rho} \cdot \nabla) U(r)|_{r=R}$$
$$+ \frac{1}{2}(\vec{\rho} \cdot \nabla)^2 U(r)|_{r=R}$$
$$+ \frac{1}{6}(\vec{\rho} \cdot \nabla)^3 U(r)|_{r=R}$$
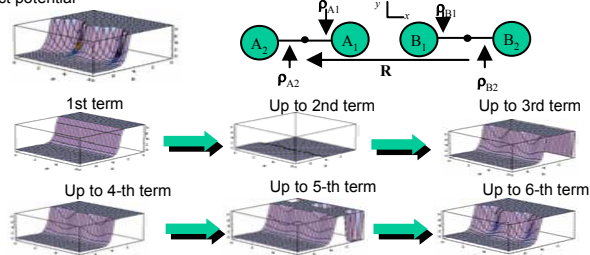$$+ \frac{1}{24}(\vec{\rho} \cdot \nabla)^4 U(r)|_{r=R}$$

real molecule

blob model

R = center-of-mass to center-of-mass distance

- ● "point" or zeroth moment
- → "dipole" or first moment
- ⟷ "quadrupole" or second moment

Construction of Inter-Blob Potentials

Ab initio* and fitted blob potentials for benzene dimer configurations.

experimental data & ab initio quantum chemistry data
→ sample configurations
→ inter-blob potential
→ **Solve Newton-Euler equations for translation and rotation.**

*Hobza et al., J. Phys. Chem. 100, 18794 (1996).

Exact potential

1st term   Up to 2nd term   Up to 3rd term
Up to 4-th term   Up to 5-th term   Up to 6-th term

Example: Coarse - graining a polycarbonate monomer

Atomistic details of a molecule
→ Selective functional groups
→ Coarse - grained model
→ Regroup relevant units
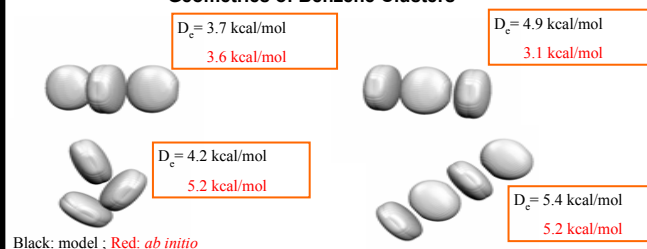→ Next-level coarse - grained model
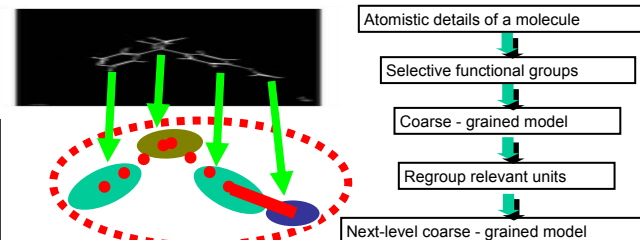
Advantages of coarse - grained rigid blob model

(1) This is NOT the conventional multipole expansion for electrostatics.
(2) In general, this method reduces the conventional $O(N^2_{atom})$ computational cost to a $O(N^2_{blob})$, while $N_{blob} \ll N_{atom}$.
(3) Unprecedented novel results for large systems can be simulated.
(4) Even though the interactions have been coarse-grained, the chemical identity and symmetry are preserved. In particular, the molecular shapes can be realized by a series of well controlled approximations.
(5) The formalism has its own mathematical structures not explored before and leads to new parallel algorithms for efficient computations.

Geometries of Benzene Clusters

$D_e = 3.7$ kcal/mol
3.6 kcal/mol

$D_e = 4.9$ kcal/mol
3.1 kcal/mol

$D_e = 4.2$ kcal/mol
5.2 kcal/mol

$D_e = 5.4$ kcal/mol
5.2 kcal/mol

Black: model ; Red: *ab initio*

Summary of present status and perspectives

- We have systematically developed a coarse-grained rigid blob model and implemented the methodology into a working program which can perform molecular dynamics simulation.
- We have applied the methodology on several generic systems. In particular, using high-quality quantum chemistry calculation data for the benzene dimer, we have constructed an inter-blob potential that can reproduce the known benzene cluster geometries and energetics within ~ 1 kcal/mol.
- A new "symmetry"-adapted formalism has also been developed which can make the best utility of molecular symmetries in simulations.
- We will apply this model in nanostructure simulations and compare the results with experiments.